CALCULATION OF THE MOLECULAR STRUCTURE OF ANILINE DERIVATIVES

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Introduction

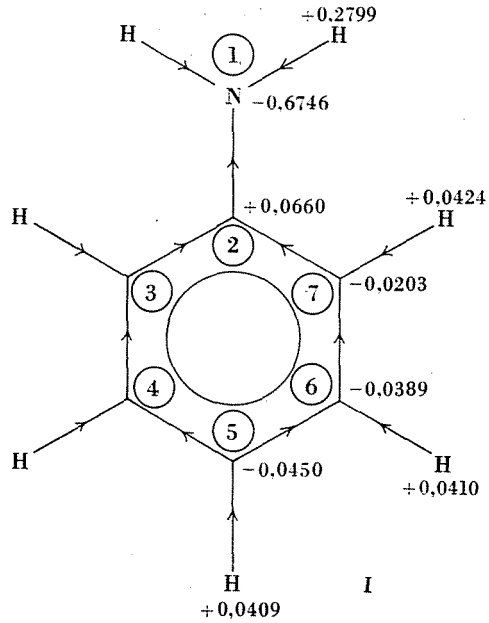
Several authors have already dealt with the calculation of the molecular structure of aniline and aniline derivatives. Calculation of the bond structure of aniline derivatives served to investigate the molecular structure of N-trimethyl-silyl-aniline derivatives. In our work the π bond systems were calculated by the Pariser—Parr—Pople method taking the σ polarization into consideration, thus, by combining the Del Re and PPP methods. Our results were compared with data from ultraviolet spectra and experimental dipole moment values. Molecular structures of the following compounds were investigated: aniline (I), N-methyl-aniline (II), N,N-dimethyl-aniline (III).

Quantum-chemical calculations

In calculating the σ bond system of molecules the approximate method of DEL RE was used [1]. The parameters, partly original and partly modified by us, necessary for the calculations, have been published in [2]. The σ charge distribution of the molecules is given in Fig. 1. The direction of bond dipole moment vectors are shown by arrows in the figure.

The π system has been calculated by the PARISER—PARR—POPLE method [3, 4]. In each compound, the valence state ionization potential of atoms was calculated as a function of effective nuclear charge defined by BURNS [5]. Our calculations have shown that the BURNS method determines the shielding factors more exactly as if calculating with the effective nuclear charges fixed according to Slater. In the course of determining the shielding parameters, promotion and hybridization states have been taken into account, too. δ_σ partial charges obtained by the DEL RE method and q_π electron populations obtained from the calculation of the π system have been considered for the calculation of the effective nuclear charge of an atom in a molecule. So the real effective nuclear charges have been calculated in the following way:

$$Z = Z^\circ + 0.35\ \delta_\sigma - 0.35\ q_\pi.$$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H
2
3
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4
6
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5
H
H
−0.0450
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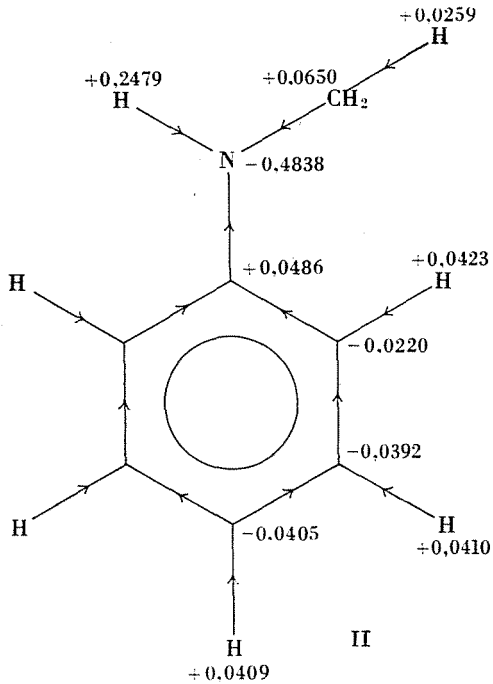
H
+0.0409

I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II

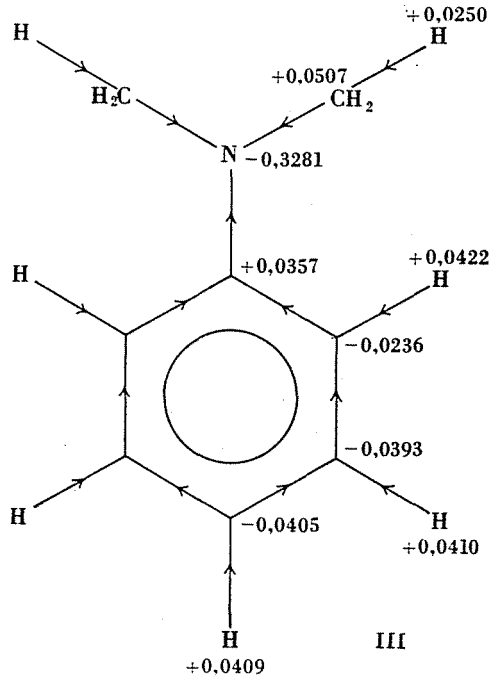

Fig. 1. σ-partial charges of aniline (I), N-methyl-aniline (II) and N,N-dimethyl-aniline (III)

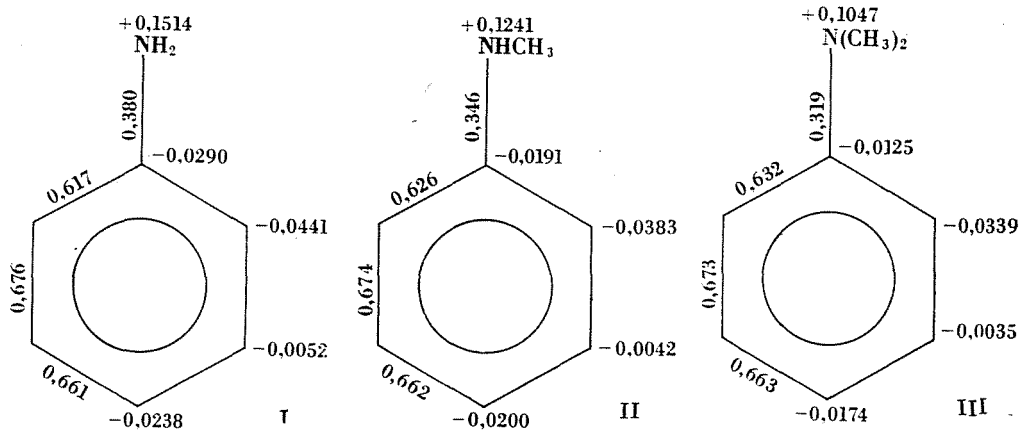

Fig. 2. π-partial charges and π bond orders of aniline (I), N-methyl-aniline (II) and N,N-dimethyl-aniline (III)

Instead of parabolic functions found in the literature, exponential functions determined by transformation were used or experimental data were started from for the calculation of ionization energies. The equations of car-

bon and nitrogen atoms are the following:

$$U_C = -0.6133 \exp (1.036\, Z)$$

$$U_{N^+} = -3.6528 \exp (0.5468\, Z)$$

Values for γ_{ii} were taken from [6]:

$$\gamma_{CC} = 11.13 \text{ eV}, \quad \gamma_{NN} = 17.44 \text{ eV}.$$

The values of γ_{ij} were calculated according to MATAGA and NISHIMOTO [7] from the bond distances.

The resonance integrals (β_{ij}) were determined by the approximate formula of WOLFSBERG and HELMHOLTZ [8] in the following way:

$$\beta_{ij} = \frac{1}{2} k(U_i + U_j)\, S_{ij}$$

where k is a proportionality factor the value of which was determined from the experimental and calculated resonance and overlapping integrals of benzene:

$$k = 0.6426.$$

S_{ij} is an overlapping integral the value of which was calculated from an integral tabulation [9] as a function of the bond distance and effective nuclear charges. Table I compiles the initial data necessary for the calculation of the π systems.

In our calculations the nitrogen atom was considered to be in sp^2 hybrid state in the three molecules. Accordingly, the bond angles of nitrogen were chosen as 120° and a planar arrangement was supposed. Bond distances were assumed [10] as:

$$R_{NH} = 1.014 \text{ Å}, \; R_{NC_{Ar}} = 1.426 \text{ Å}, \; R_{NC_{Alk}} = 1.474 \text{ Å},$$

$$R_{CC} = 1.397 \text{ Å}, \; R_{C_{Ar}H} = 1.084 \text{ Å}, \; R_{C_{Alk}H} = 1.093 \text{ Å}.$$

The calculations were carried out on a computer RAZDAN-3. The Z_i, U_i and α_i values were changed using the results obtained in the 0^{th} approximation, but the β_{ij} values were considered to be constant. The approximations were continued to self-consistence. The eigenvalues, linear coefficients, partial charges, electron densities and bond orders for the examined compounds were determined. Configuration interactions were taken into consideration, too, and by the aid of these interactions the values of singlet and triplet

Table 1

Initial data for calculation of π-bond system of aniline-derivatives with PPP method

	I.	II.	III.
Z_1	4.264	4.331	4.385
Z_2	3.173	3.167	3.163
Z_3	3.143	3.142	3.142
Z_4	3.136	3.136	3.136-
Z_5	3.136	3.136	3.136
U_1 (eV)	−25.637	−26.591	−27.396
U_2	−11.430	−11.358	−11.306
U_3	−11.078	−11.071	−11.064
U_4	−11.004	−11.003	−11.002
U_5	−10.997	−10.997	−10.997
β_{12} (eV)	− 2.1845	− 2.1899	− 2.1855
β_{23}	− 2.4109	− 2.4147	− 2.4084
β_{34}	− 2.4015	− 2.4006	− 2.3997
β_{45}	− 2.3927	− 2.3926	− 2.3924

transition energies as well as oscillator strengths were determined. The calculation results are presented in Fig. 2, Tables 2 and 3.

Discussion

The bond polarities, bond moments, μ_σ and μ_π dipole moment and resultant dipole moment of the compound were calculated from the σ and π charge

Table 2

Eigenvalues of aniline-derivatives

(eV)	I.	II.	III.
E_1	−13.5225	−13.6502	−13.7816
E_2	−11.3935	−11.6465	−11.8860
E_3	− 9.9615	−10.0021	−10.0303
E_4	− 8.6564	− 8.9614	− 9.1817
E_5	− 0.4003	− 0.4462	− 0.4782
E_6	− 0.2552	− 0.3102	− 0.3564
E_7	2.6342	2.5932	2.5574

Table 3

Values of singlet ($^1E_{CI}$) and triplet ($^3E_{CI}$) transition-energies and oscillator strengths for aniline derivatives

	$^1E_{CI}$(eV)	f	$^3E_{CI}$ (eV)
I.	4.4334	0.044	2.8222
	5.3496	0.393	3.4939
	6.2965	0.420	3.7664
	6.6909	0.805	4.8337
	7.5866	0.665	5.8202
	7.8297	0.189	6.4295
II.	4.5716	0.033	2.9357
	5.5392	0.324	3.6354
	6.4807	0.598	3.8314
	6.7218	0.894	4.8424
	7.7247	0.506	6.1545
	7.9329	0.140	6.6249
III.	4.6556	0.024	2.9906
	5.6808	0.261	3.7253
	6.6194	0.766	3.8745
	6.7552	0.980	4.8469
	7.8826	0.349	6.4346
	8.0379	0.097	6.7720

distribution of molecules. The calculated dipole moments are compared with experimental values in Table 4.

The experimental ultraviolet absorption data of the aniline derivatives are compared with the calculated values of singlet and triplet transitions and oscillator strengths. For sake of comparison, the figure shows a few results by other authors.

Tables 4 and 5 show a good agreement between experimental and cal-

Table 4

Calculated and experimental dipole moments of aniline-derivatives

	μ_σ (D)	μ_π (D)	$\mu_{\sigma\pi}$ (D)	μ_{exp} [11] (D)	Δ (D)
I.	0.176	1.757	1.933	1.56	−0.37
II.	0.163	1.460	1.615	1.67	+0.05
III.	0.125	1.249	1.374	1.57	+0.20

Table 5

Experimental and calculated singlet transitions (in eV) and oscillator strengths of aniline-derivatives

	$^1E_{CI}$ (f) experimental	$^1E_{CI}$ (f) calculated by us	Difference (eV)	Data calculated by other authors					
				[14]	[15]	[16]	[17]	[18]	[6]
	4.40 (0.028) [12]	4.43 (0.044)	−0.03	4.37 (0.05)	4.39 (0.048)	4.38 (0.048)	4.31 (0.083)	4.39 (0.05)	4.39 (0.075)
	5.39 (0.144)	5.35 (0.393)	+0.04	5.35 (0.34)	5.50 (0.264)	5.50 (0.265)	5.30 (0.485)	5.28 (0.38)	5.43 (0.316)
I.	6.40 (0.510)	6.30 (0.420)	+0.10	6.35 (0.55)	6.40 (0.732)	6.40 (0.729)	6.68 (0.787)	6.33 (0.54)	6.36 (0.606)
	6.88 (0.570)	6.69 (0.805)	+0.19	6.55 (0.87)	6.60 (1.085)	6.59 (1.064)	6.74 (1.028)	6.50 (0.82)	6.63 (1.034)
	7.87 (0.680)	7.59 (0.665)	+0.28		7.66 (0.295)	7.65 (0.295)			
		7.83 (0.189)			7.70 (0.008)				
	4.20 [13]	4.57 (0.033)	−0.37	4.09 (0.07)					
	5.10	5.54 (0.324)	−0.44	5.08 (0.46)					
II.		6.48 (0.598)		6.07 (0.27)					
		6.72 (0.894)		6.49 (0.76)					
		7.72 (0.506)							
		7.93 (0.140)							
	4.30 (0.044) [12]	4.66 (0.024)	−0.36	3.98 (0.08)	4.23 (0.065)				
	5.15 (0.256)	5.68 (0.261)	−0.53	5.01 (0.50)	5.33 (0.348)				
III.	6.25 (0.350)	6.62 (0.766)	−0.37	6.01 (0.22)	6.27 (0.540)				
	6.88 (0.575)	6.76 (0.980)	+0.12	6.48 (0.74)	6.59 (1.044)				
	7.68 (0.810)	7.88 (0.349)	−0.20		7.48 (0.453)				
		8.04 (0.097)			7.49 (0.016)				

culated values for both dipole moment and ultraviolet data. This fact proves that the applied Del Re and PPP methods supply proper values for the molecular structure of aniline derivatives.

Summary

Quantum-chemical calculations were made for various aniline derivatives. For calculating the σ- and π-bond systems the Del Re method and the Pariser—Parr—Pople method, respectively, were used, taking the σ-polatization into account. The results show a good agreement for the experimental dipole moments and the data of ultraviolet spectra.

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